

CLAIMS

1. A recording method wherein an ink composition comprising at least a colorant, resin emulsion particles, a water-soluble organic solvent, and water and a reaction solution comprising a reactant capable of forming coagulate upon contact with the ink composition, are deposited onto a recording medium to perform printing, said recording method comprising the steps of:

depositing the reaction solution onto the recording medium;

depositing the ink composition onto the recording medium to record an image; and

washing the recording medium, on which the reaction solution and the ink composition have been deposited to perform printing, with a polar solvent.

2. The recording method according to claim 1, wherein the recording medium is substantially non-absorptive to the ink composition.

3. The recording method according to claim 1, wherein the recording medium has a plastic, rubber, metallic, or ceramic surface.

4. The recording method according to any one of claims 1 to 3, wherein the colorant is a pigment or a dye.

5. The recording method according to any one of claims 1 to 3, wherein the colorant comprises: a dye or a pigment; and a polymer which has in its molecular chain sites possessing ultraviolet absorbing activity and/or photostabilizing activity and in which the dye or the pigment has been included, the colorant being in a fine particle form.

6. The recording method according to claim 5, wherein the site possessing ultraviolet absorbing activity and/or photostabilizing activity is selected from the group consisting of aromatic monocyclic hydrocarbon, fused polycyclic aromatic hydrocarbon,

heteromonocyclic, and fused heterocyclic groups and has absorption in the wavelength range of 200 to 400 nm.

7. The recording method according to claim 5, wherein the site possessing ultraviolet absorbing activity or photostabilizing activity has a benzotriazole, benzophenone, salicylate, cyanoacrylate, hindered phenol, or hindered amine skeleton.

8. The recording method according to claim 5, wherein the polymer is a homo- or co-polymer of a benzotriazole ultraviolet absorber having an ethylenically unsaturated bond, a benzophenone ultraviolet absorber having an ethylenically unsaturated bond, a salicylate ultraviolet absorber having an ethylenically unsaturated bond, a cyanoacrylate ultraviolet absorber having an ethylenically unsaturated bond, a hindered phenol ultraviolet absorber having an ethylenically unsaturated bond, or a hindered amine photostabilizer having an ethylenically unsaturated bond as a monomer.

9. The recording method according to claim 5, wherein the polymer is composed mainly of a thermoplastic polymer.

10. The recording method according to claim 5, wherein the thermoplastic polymer is selected from the group consisting of ethylene-vinyl acetate copolymers, ethylene-ethyl acrylate copolymers, polyethylene, polypropylene, polystyrene, poly(meth)acrylic esters, styrene-(meth)acrylic ester copolymers, styrene-malelic acid copolymers, styrene-itaconic ester copolymers, polyvinyl acetates, polyesters, polyurethanes, and polyamides.

11. The recording method according to claim 5, wherein the polymer has a carboxyl group or a sulfonic acid group as a functional group.

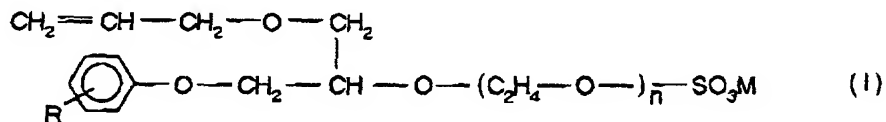
12. The recording method according to claim 4, wherein the colorant has a particle diameter of 5 to 500 nm.

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13. The recording method according to claim 4, wherein the content of the dye or the pigment is 0.1 to 99% by weight based on the colorant.

14. The recording method according to any one of claims 1 to 3, wherein the colorant is a water-based pigment dispersion which comprises a pigment included in a polymer produced from a polymerizable surfactant having both nonionic hydrophilicity and anionic hydrophilicity and a monomer.

15. The recording method according to claim 14, wherein the polymerizable surfactant is a compound represented by formula (I):



wherein

R represents a hydrogen atom or a hydrocarbon residue having 1 to 12 carbon atoms;

n is a number of 2 to 20; and

M represents an alkali metal atom, an ammonium salt, or an alkanolamine.

16. The recording method according to claim 14, wherein the water-based pigment dispersion has been produced by dispersing a pigment in water and/or a water-soluble organic solvent with the aid of a polymerizable surfactant, adding a monomer and a polymerization initiator to the dispersion, and then polymerizing the mixture.

17. The recording method according to claim 16, wherein the water-based pigment dispersion has been produced by further performing wet grinding after the polymerization.

18. The recording method according to claim 14, wherein the monomer is an electron-accepting monomer.

19. The recording method according to claim 14,

wherein the monomer is selected from the group consisting of diesters of fumaric acid, diesters of maleic acid, maleimides, and vinylidene cyanide.

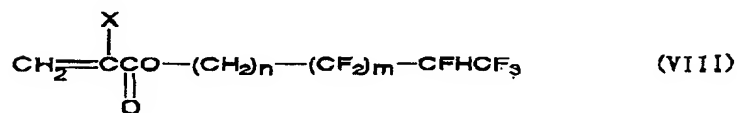
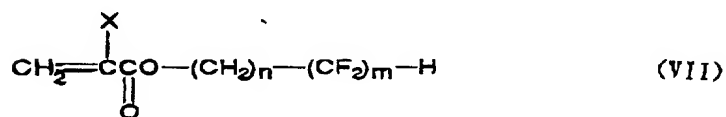
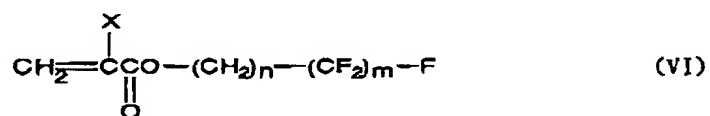
20. The recording method according to claim 14, wherein the monomer is selected from the group consisting of acrylic acid, acrylic esters, methacrylic acid, and methacrylic esters.

21. The recording method according to claim 14, wherein the content of the water-based pigment dispersion is 1 to 20% by weight based on the ink composition.

22. The recording method according to any one of claims 1 to 3, wherein the resin emulsion particles are formed of a polymer comprising a fluoroalkyl-containing monomer.

23. The recording method according to claim 22, wherein the fluoroalkyl group is such that 3 to 41 fluorine atoms are present in a straight-chain or branched alkyl group having 1 to 13 carbon atoms.

24. The recording method according to claim 22, wherein the fluoroalkyl-containing monomer is selected from the group consisting of compounds represented by formulae (VI) to (VIII):



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wherein

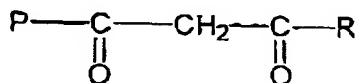
n is 1 or more; and

m is 1 to 20.

25. The recording method according to any one of claims 1 to 3, wherein the resin emulsion particles are formed of a polymer having a ligand structure, which can combine with a metal ion to form a chelate, and, upon combining with the metal ion to form a chelate, form coagulate.

26. The recording method according to claim 25, wherein the ligand structure, which can combine with the metal ion to form a chelate, is selected from the group consisting of  $\beta$ -diketone, polyamine, iminodiacetic acid, sarcosine, ethanolamino acid, glycine, xanthogenic acid, amidoxime, amine, pyridine, imidazole, phosphonic acid, phosphinic acid, phosphoric acid, Schiff base, oxime, hydroxame, aminopolycarboxylic acid, thiol, polythioalcohol, 2-pyrrolidone, and 2-oxazolidone structures.

27. The recording method according to claim 25, wherein the ligand structure, which can combine with the metal ion to form a chelate, is represented by the following formula:



wherein

P represents a polymer structure portion; and

R represents an alkyl or aryl group.

28. The recording method according to any one of claims 1 to 3, wherein the resin emulsion particles are comprised of a polymer having a film-forming property.

29. The recording method according to any one of claims 1 to 3, wherein the content of the resin emulsion particles is 0.1 to 30% by weight based on the ink composition.

30. The recording method according to any one of claims 1 to 3, wherein the resin emulsion particles have a diameter of not more than 400 nm.

31. The recording method according to any one of claims 1 to 3, wherein the resin emulsion particles have a glass transition point of 20°C or below.

32. The recording method according to any one of claims 1 to 3, wherein the resin emulsion containing the resin emulsion particles have a minimum film-forming temperature of 30°C or below.

33. The recording method according to any one of claims 1 to 3, wherein the resin emulsion particles have a film-forming property and have a reactivity with a divalent metal salt such that, when 3 volumes of a resin emulsion containing 0.1% by weight of the resin emulsion particles is brought into contact with one volume of a 1 mol/liter aqueous divalent metal salt solution, the time required for the transmission of light having a wavelength of 700 nm to become 50% of the initial value is not more than  $1 \times 10^4$  sec.

34. The recording method according to claim 33, wherein the resin emulsion particles have carboxyl groups on the surface thereof.

35. The recording method according to any one of claims 1 to 3, wherein a resin emulsion, which has been prepared so as to contain 10% by weight of the resin emulsion particles, has a contact angle on a teflon sheet of not less than 70 degrees.

36. The recording method according to any one of claims 1 to 3, wherein the resin emulsion particles have at least one functional group selected from the group consisting of carboxyl, sulfone, amide, amino, and hydroxyl groups.

37. The recording method according to any one of claims 1 to 3, wherein a resin emulsion, which has been prepared so as to contain 35% by weight of the resin emulsion particles, has a surface tension of not less

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than  $40 \times 10^{-3}$  N/m ( $20^{\circ}\text{C}$ ).

38. The recording method according to any one of claims 1 to 3, wherein the resin emulsion particles contain 1 to 10% by weight of a structure derived from an unsaturated vinyl monomer having a carboxyl group and have a structure crosslinked by a crosslinkable monomer having two or more polymerizable double bonds with the content of the structure derived from the crosslinkable monomer being 0.2 to 4% by weight.

39. The recording method according to any one of claims 1 to 3, wherein the resin emulsion particles have a core-shell structure.

40. The recording method according to claim 39, wherein the core is formed of an epoxy-containing resin and the shell is formed of a carboxyl-containing resin.

41. The recording method according to claim 40, wherein the shell has at least one functional group selected from the group consisting of carboxyl, sulfone, amide, amino, and hydroxyl groups.

42. The recording method according to any one of claims 1 to 3, wherein the resin emulsion particles are self-crosslinkable.

43. The recording method according to any one of claims 1 to 3, wherein the ink composition further comprises a sequestering agent.

44. The recording method according to claim 43, wherein the sequestering agent is an aminocarboxylic acid derivative or a condensed phosphoric acid.

45. The recording method according to claim 43, wherein the sequestering agent is selected from the group consisting of ethylenediaminetetraacetic acid, iminodiacetic acid, nitriloacetic acid, diethylenetriaminepentaacetic acid, triethylenetetraminehexaacetic acid, cyclohexane-1,2-diaminetetraacetic acid, N-hydroxyethylethylenediaminetriacetic acid, ethylene glycol diethyl ether amine tetraacetic acid,

ethylenediaminetetrapropionic acid, pyrophosphoric acid, and triphosphoric acid.

46. The recording method according to claim 43, wherein the sequestering agent is contained in an amount of 0.0001 to 5% by weight based on the ink composition.

47. The recording method according to any one of claims 1 to 3, wherein the water-soluble organic solvent has a boiling point of 180°C or above.

48. The recording method according to any one of claims 1 to 3, wherein the reactant is a polyvalent metal salt, a polyallylamine, or a polyallylamine derivative.

49. The recording method according to claim 48, wherein the polyvalent metal salt is a nitrate or a carboxylate.

50. The recording method according to claim 49, wherein carboxylic acid ions constituting the carboxylate have been derived from a saturated aliphatic monocarboxylic acid having 1 to 6 carbon atoms, wherein hydrogen atoms on the saturated aliphatic hydrocarbon group in the monocarboxylic acid are optionally substituted by a hydroxyl group, or a carbocyclic monocarboxylic acid having 6 to 10 carbon atoms.

51. The recording method according to any one of claims 1 to 3, wherein the reactant comprises cationic inorganic fine particles and/or fine particles of a cationic polymer.

52. The recording method according to claim 51, wherein the cationic inorganic fine particles have been cationized by hydrating inorganic fine particles, or by treating inorganic fine particles with a cationic material.

53. The recording method according to claim 51, wherein the inorganic fine particles are inorganic colloid particles.

54. The recording method according to claim 52, wherein the cationic material is an alumina sol, a

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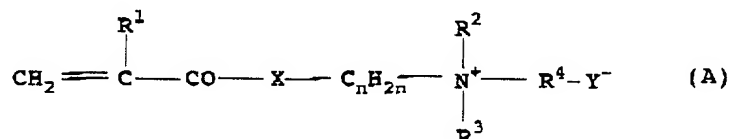
alumina chloride, a cationic surfactant, or a polycation compound.

55. The recording method according to claim 51, wherein the cationic inorganic fine particles are a cationic alumina sol or a cationic colloidal silica.

56. The recording method according to claim 51, wherein the fine particles of a cationic polymer have been produced by treating fine particles of a polymer with a cationic material to cationize the fine particles, or by polymerizing a cationic monomer.

57. The recording method according to claim 51, wherein the fine particles of a cationic polymer are formed of a polymer selected from the group consisting of acrylic resins, polyester resins, epoxy resins, styrene-butadiene copolymers, polybutadienes, polyolefins, polystyrenes, polyamides, ethylene-vinyl acetate copolymers, polysiloxanes, and polyurethanes.

58. The recording method according to claim 51, wherein the fine particles of a cationic polymer are fine particles formed of a polymer produced by copolymerizing a cationic monomer represented by formula (A) and a vinyl monomer:



wherein

$\text{R}^1$  represents a hydrogen atom or a methyl group;

$\text{X}$  represents an oxygen atom or an NH group;

$\text{R}^2$  and  $\text{R}^3$  each independently represent a straight-chain or branched alkyl group having 1 to 4 carbon atoms;

$\text{R}^4$  represents a hydrogen atom or an optionally substituted straight-chain or branched alkyl group having 1 to 4 carbon atoms;

$n$  is an integer of 2 to 5; and

$\text{Y}^-$  represents a salt forming anion.

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59. The recording method according to any one of claims 1 to 3, wherein the reaction solution further comprises triethylene glycol monobutyl ether and glycerin.

60. The recording method according to any one of claims 1 to 3, wherein the step of depositing droplets of the ink composition on the recording medium is carried out after the step of depositing the reaction solution on the recording medium.

61. The recording method according to any one of claims 1 to 3, wherein the step of depositing droplets of the ink composition on the recording medium is carried out before the step of depositing the reaction solution on the recording medium.

62. The recording method according to any one of claims 1 to 3, wherein the step of depositing droplets of the ink composition on the recording medium or the step of depositing the reaction solution on the recording medium is an ink jet recording method wherein droplets are ejected and deposited on the recording medium to perform printing.

63. The recording method according to any one of claims 1 to 3, wherein the printing is real image printing and/or mirror image printing.

64. The recording method according to claim 1, wherein the recording medium is an industrial product, an industrial article, a domestic electric appliance, an article for buildings, furniture, tableware, an aircraft, a vehicle, a ship, a card, a packaging container, a medical supply or device, clothing, boots or shoes, a bag, an office supply, stationery, a toy, a sign, or a fiber.

65. A record produced by printing according to the recording method as defined in any one of claims 1 to 3.

66. A method for providing text information, image information, or design on a recording medium by the recording method according to any one of claims 1 to 3.

67. A recording apparatus for depositing an ink composition and a reaction solution containing a reactant, which forms coagulate upon contact with the ink composition, onto a recording medium to perform printing,

the ink composition and the reaction solution being the ink composition and the reaction solution for use in the recording method according to any one of claims 1 to 56,

said recording apparatus comprising:

means for depositing the reaction solution onto the recording medium;

means for depositing the ink composition onto the recording medium to record an image;

means for controlling the means for depositing the reaction solution onto the recording medium and the means for depositing the ink composition onto the recording medium to record an image; and

means for washing the recording medium, on which the reaction solution and the ink composition have been deposited to perform printing, with a polar solvent.

68. The recording apparatus according to claim 67, wherein the means for controlling the means for depositing the reaction solution onto the recording medium and the means for depositing the ink composition onto the recording medium to record an image are ink jet recording means.

69. The recording apparatus according to claim 67 or 68, wherein the printing is real image printing and/or mirror image printing.

70. A record produced by printing using the recording apparatus according to any one of claims 67 to 69.

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